Influence of electron and phonon temperature on the efficiency of thermoelectric conversion

A. Sellitto*[†] and V. A. Cimmelli[‡]
Department of Mathematics, Computer Science and Economics,
University of Basilicata, Campus Macchia Romana, 85100, Potenza, Italy

D. Jou[§]
Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain and
Institut d'Estudis Catalans, Carme 47, Barcelona 08001, Catalonia, Spain

(Dated: February 28, 2021)

In the framework of Extended Irreversible Thermodynamics it is developed a two-temperature model (for electrons and phonons, respectively) of thermoelectric effects. The expression of the maximum efficiency in terms of these two temperatures is derived as well. It is proved that, for the electron temperature higher than the phonon temperature, the two-temperature model yields an efficiency which is higher with respect to that of the single-temperature model. Two possible experiments to estimate the electron temperature are suggested.

PACS numbers: 44.10.+i,66.70.-f,05.70.Ln
Keywords: Second Kelvin relation; thermoelectric effects; Onsager reciprocal relations; phonon drag; thermoelectric efficiency

Nomenclature

c_v specific heat at constant volume

$c_v^{(e)}$ specific heat at constant volume of electrons

$c_v^{(p)}$ specific heat at constant volume of phonons

$\mathbf{E}$ electric-field vector

$\mathbf{i}$ electric-current density vector

$\mathbf{J}^{(s)}$ specific-entropy flux vector

$\mathbf{q}$ overall local heat-flux vector

$\mathbf{q}^{(e)}$ local heat-flux vector due to electrons

$\mathbf{q}^{(p)}$ local heat-flux vector due to phonons

s specific entropy

T average temperature

T_e electrons temperature

T_p phonons temperature

u specific internal energy

u_e specific internal energy of electrons

---

* Corresponding author
[†] Electronic address: `ant.sellitto@gmail.com`
[‡] Electronic address: `vito.cimmelli@unibas.it`
[§] Electronic address: `david.jou@uab.cat`

u_p specific internal energy of phonons

Z figure-of-merit

Greek symbols

ϵ Seebeck coefficient

η thermoelectric efficiency

λ total thermal conductivity

λ_e electrons thermal conductivity

λ_p phonons thermal conductivity

μ_e electron chemical potential

Π Peltier coefficient

ρ mass density

$\varrho^{(e)}$ specific electric charge

Σ thermodynamic state space

σ_e electrical conductivity

$\sigma^{(s)}$ rate of entropy-density production

τ_e relaxation time of electrons

τ_i relaxation time of electric charges

τ_p relaxation time of phonons

Subscripts

e electrons

eff effective

i electric-current density

max maximum

p phonons

Superscripts

(e) electrons

(p) phonons

(s) entropy

I. INTRODUCTION

Thermoelectricity is actually viewed as a very interesting source of electric power because of its ability to convert heat flow directly into electricity. In particular, thermoelectric devices as energy converters are easily scalable and do not have moving parts, or liquid fuels. These excellent features make them applicable in almost any situation where large quantities of heat tend to go to waste, from clothing to large industrial facilities.

Whilst the thermoelectric materials have been known and understood for quite some time, so far they have not been efficient enough to be used commercially. Currently, many research groups are investing their efforts in finding new materials with appropriate properties to better use thermoelectric effects, creating so efficient thermoelectric devices. A good thermoelectric material will have very poor thermal conductivity λ, but a very high electrical conductivity σ_e, so that the so-called figure-of-merit $Z = \epsilon^2\sigma_e/\lambda$, with ϵ being the Seebeck coefficient, which is the main responsible of the thermoelectric efficiency, is as high as possible.

Indeed, the advent of nanotechnology is widening the range of applicability of thermoelectric materials. In fact, the nanostructures used in materials maintain good electrical conductivity, while reducing the thermal conductivity. The performances of thermoelectric devices can thus be enhanced with the use of nanotechnology-based materials that have improved thermoelectric properties and good solar energy absorption abilities. Thermoelectric materials based on $\mathrm{Bi_2\,Te_3}$, for example, stand out as perfect examples highlighting the role of nanomaterials for thermoelectric devices. Carbon nanotubes and graphene sheets as thermoelectric materials also exhibit improved thermoelectric properties. In general, the usage of nanostructures smaller than the wavelength of light enhances the scattering of photons decreasing so the thermal conductivity. This decreasing in the thermal conductivity seems to be the most vital benefit of nanostructuring for thermoelectric materials.

Although it is very clear the importance of using nanotechnology in thermoelectricity, the design of good thermoelectric nanodevices is still far from its optimal solution. This principally because the physics at nanoscale presents some dark points, as for instance the role played by memory, nonlocal and nonlinear effects, as well as the appropriate definition of temperature in nonequilibrium situations [1–5].

In Ref. [6] we have investigated the influence of nonlocal effects on the figure-of-merit in cylindrical nanowires, and predicted how it depends on the features of the transversal section. In the present paper, instead, we focus our attention especially on the role of the temperature and on the possibility of accounting for different values for electron and phonon temperature. Our investigation starts by the observation that, as the electron mean-free path ℓ_e is usually shorter than the phonon mean-free path ℓ_p, when heat propagates in a system whose characteristic size L is such that $\ell_e < L < \ell_p$, it is expected a very high number of electron collisions, and only scant phonon collisions. This yields that the electron temperature T_e may reach its local-equilibrium value, whereas the phonon temperature T_p is still far from its own local-equilibrium value. Conversely, when the electron mean-free path (corresponding to the electron-phonon collisions) is large, one may have the so-called phenomenon of "hot electrons", namely, a population of electrons whose average kinetic energy (i.e., the kinetic temperature) is considerably higher than that of the phonons [7, 8]. Another situation in which it is possible to have different temperatures for phonons and electrons is when a high-frequency electromagnetic radiation is used to supply energy to the system, since in such a case the electrons receive energy at a rate higher than that at which they give energy to the phonons. Therefore, it would be interesting to find possible ways to measure both temperatures [9, 10].

Besides being appealing from the theoretical point of view, accounting for two different temperatures is also important in practical applications, since it leads to a more realistic computation of the thermodynamic efficiency of the thermoelectric devices.

Here we develop a mesoscopic model of enhanced thermoelectric equations which account for different phonon and electron temperatures. Following the way drawn in Refs. [6, 11], we also assume that the overall heat flux $\mathbf{q}$ has two different contributions: the phonon heat flux $\mathbf{q}^{(p)}$ and the electron heat flux $\mathbf{q}^{(e)}$, in such a way that $\mathbf{q} = \mathbf{q}^{(p)} + \mathbf{q}^{(e)}$.

The layout of the paper is the following. In Sec. II, we develop a theoretical model describing thermoelectric effects when the electrons and the phonons do not have the same temperature. As a consequence of the second Kelvin relation, we suggest a possible way to measure those temperatures. In Sec. III, as a practical application of that model, we determine the efficiency of a thermoelectric generator. We point out that the difference between electron and phonon temperature can contribute to improve the thermoelectric efficiency. In Sec. IV we draw the main conclusions and we underline that our model may also cope with the phonon-drag phenomenon, suggesting so a further experiment to check both the electron and the phonon temperature.

II. THE PHENOMENOLOGICAL LAWS

The analysis of coupled transport processes is one of the outstanding aspects of the classical theory of nonequilibrium thermodynamics [3, 12]. In the present section we aim to derive the phenomenological laws describing the thermoelectric effects whenever the different heat carriers (i.e., the phonons and the electrons in our case) no longer have the same temperature.

Since we assume that the heat carriers behave as a mixture of gases flowing through the crystal lattice [13, 14], it seems logical to suppose that the internal energy of phonons per unit mass u_p, the internal energy of electrons per unit mass u_e and the electrical charge per unit mass of electrons $\varrho^{(e)}$ belong to the state space. In particular, we assume that those state-space variables are ruled by the following evolution equations:

$$\rho \partial_t u_p = -\nabla \cdot \mathbf{q}^{(p)} \tag{1a}$$

$$\rho \partial_t u_e = -\nabla \cdot \mathbf{q}^{(e)} + \mathbf{E} \cdot \mathbf{i} \tag{1b}$$

$$\rho \partial_t \varrho^{(e)} = -\nabla \cdot \mathbf{i} \tag{1c}$$

with ρ as the mass density, $\mathbf{E}$ as the electric field, and $\mathbf{i}$ as the electric-current density [6]. We note that the summation of Eqs. (1a) and (1b) turns out the well-known energy-balance equation

$$\rho \partial_t u + \nabla \cdot \mathbf{q} = \mathbf{E} \cdot \mathbf{i}$$

obtained in Ref. [15] in the absence of a magnetic field, once the total internal energy per unit mass of the system u is supposed to be given by the constitutive relation

$$u = u_p + u_e \tag{2}$$

According with the basic principles of Extended Irreversible Thermodynamics (EIT) [3, 5], we may assume that the fluxes of previous unknown variables (namely, $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$ and $\mathbf{i}$) are the other state-space variables. Elevating the fluxes to the status of independent variables amounts to introduce memory and nonlocal effects into the formalism [16, 17].

In the Appendix at the end of the paper it is shown that, whenever the relaxation times of those fluxes are negligible, the choice above of the state-space variables implies that the specific entropy s is such that $s = s\left(u_p; u_e; \varrho^{(e)}\right)$. Therefore, in that case, from the Gibbs relation between s and the state variables, we have

$$\mathrm{d}s = \frac{\partial s}{\partial u_p}\mathrm{d}u_p + \frac{\partial s}{\partial u_e}\mathrm{d}u_e + \frac{\partial s}{\partial \varrho^{(e)}}\mathrm{d}\varrho^{(e)} \Rightarrow \partial_t s = \frac{1}{T_p}\partial_t u_p + \frac{1}{T_e}\partial_t u_e - \frac{\mu_e}{\varrho^{(e)} T_e}\partial_t \varrho^{(e)} \tag{3}$$

wherein $T_p = \left(\partial s/\partial u_p\right)^{-1}$, $T_e = \left(\partial s/\partial u_e\right)^{-1}$, and $\mu_e / \left(\varrho^{(e)} T_e\right) = -\partial s/\partial \varrho^{(e)}$, μ_e being the chemical potential of the electrons.

Although Eq. (3) does not present any problem from the theoretical point of view, from the practical point of view, instead, it may lead to some perplexities due to the presence of T_p and T_e therein. In fact, one may naturally wonder whether they are measurable quantities, or not [9, 10]. Referring the readers to the end of the present section for a first possible answer to that question, now let us only observe that we are allowed to postulate the following further constitutive equations which relate the partial internal energies appearing in Eqs. (1) to those temperatures:

$$u_p = c_v^{(p)} T_p \tag{4a}$$

$$u_e = c_v^{(e)} T_e \tag{4b}$$

wherein $c_v^{(p)}$ and $c_v^{(e)}$ are the phonon and the electron specific heats at constant volume [18], respectively. As a consequence of Eqs. (4), since the total internal energy u can be expressed through the average temperature T as $u = c_v T$, being $c_v = c_v^{(p)} + c_v^{(e)}$ the specific heat at constant volume of the whole system [19], from the coupling of Eqs. (2) and (4) we obtain

$$T = \frac{c_v^{(p)} T_p + c_v^{(e)} T_e}{c_v} \tag{5}$$

which states a very strict link between T_p, T_e and T, the latter being a measurable quantity in practical applications. Note that in the very general case $c_v^{(p)}$ and $c_v^{(e)}$ should be temperature-dependent functions, but here we deal only with the simplest situation in which those material functions are constant, in order to emphasize the essential physical ideas and their consequences.

In few words, we regard the phonons and electrons as a mixture of gases flowing through the crystal lattice [13, 14], each of which is endowed with its own temperature. In this way, according with the theory of fluid mixtures with different temperatures [20–22], we are allowed to assume that each constituent obeys the same balance laws as a single fluid, and it has its own temperature. The average temperature of the mixture has been introduced by the consideration that the internal energy of the mixture is the same as in the case of a single-temperature mixture [21].

The substitution of Eqs. (1) into Eq. (3) leads to

$$\begin{aligned}\rho\partial_t s =& -\frac{\nabla\cdot\mathbf{q}^{(p)}}{T_p}-\frac{\nabla\cdot\mathbf{q}^{(e)}}{T_e}+\frac{\mu_e}{\varrho^{(e)}T_e}\nabla\cdot\mathbf{i}+\frac{\mathbf{E}\cdot\mathbf{i}}{T_e}=\\ & -\nabla\cdot\left(\frac{\mathbf{q}^{(p)}}{T_p}+\frac{\mathbf{q}^{(e)}}{T_e}-\frac{\mu_e}{\varrho^{(e)}T_e}\mathbf{i}\right)\\ & -\frac{\mathbf{q}^{(p)}\cdot\nabla T_p}{T_p^2}-\frac{\mathbf{q}^{(e)}\cdot\nabla T_e}{T_e^2}-\frac{\mathbf{i}}{T_e}\nabla\left(\frac{\mu_e}{\varrho^{(e)}}\right)+\left(\frac{\mu_e}{\varrho^{(e)}T_e^2}\right)\mathbf{i}\cdot\nabla T_e+\frac{\mathbf{E}\cdot\mathbf{i}}{T_e}\end{aligned}\tag{6}$$

Recalling that the time rate of the specific entropy has to obey the balance law

$$\rho\partial_t s=-\nabla\cdot\mathbf{J}^{(s)}+\sigma^{(s)}\tag{7}$$

with $\mathbf{J}^{(s)}$ being the entropy flux, and $\sigma^{(s)}$ the entropy source, the comparison between Eqs. (6) and (7) leads to the following identifications:

$$\mathbf{J}^{(s)}=\frac{\mathbf{q}^{(p)}}{T_p}+\frac{\mathbf{q}^{(e)}}{T_e}-\frac{\mu_e}{\varrho^{(e)}T_e}\mathbf{i}\tag{8a}$$

$$\begin{aligned}\sigma^{(s)}&=-\frac{1}{T_p}\left\{\mathbf{q}^{(p)}\cdot\frac{\nabla T_p}{T_p}\right\}-\frac{1}{T_e}\left\{\left[\mathbf{q}^{(e)}-\frac{\mu_e}{\varrho^{(e)}}\mathbf{i}\right]\cdot\frac{\nabla T_e}{T_e}\right\}+\frac{1}{T_e}\left\{\mathbf{i}\cdot\left[\mathbf{E}-\nabla\left(\frac{\mu_e}{\varrho^{(e)}}\right)\right]\right\}\\ &=\sum_\alpha\mathbf{J}^{(\alpha)}\cdot\mathbf{X}^{(\alpha)}\end{aligned}\tag{8b}$$

wherein $\mathbf{J}^{(\alpha)}$ is the thermodynamic flux, and $\mathbf{X}^{(\alpha)}$ is its conjugated thermodynamic force [3, 12].

Experience indicates that $\mathbf{J}^{(\alpha)}$ and $\mathbf{X}^{(\alpha)}$ are not independent, but that there exists a relationship between them. Moreover, it has been observed that, for a large class of irreversible processes, the thermodynamic fluxes are linear functions of the forces, to a good approximation [5, 12, 23]. This observation, which is also the simplest way to ensure that $\sigma^{(s)}$ is a non-negative quantity whatever the thermodynamic process is, allows us to write the following phenomenological relations for the fluxes appearing in our theoretical model:

$$-\mathbf{q}^{(p)}=L_{11}\frac{\nabla T_p}{T_p}+L_{12}\frac{\nabla T_e}{T_e}+L_{13}\left[\mathbf{E}-\nabla\left(\frac{\mu_e}{\varrho^{(e)}}\right)\right]\tag{9a}$$

$$\frac{\mu_e}{\varrho^{(e)}}\mathbf{i}-\mathbf{q}^{(e)}=L_{21}\frac{\nabla T_p}{T_p}+L_{22}\frac{\nabla T_e}{T_e}+L_{23}\left[\mathbf{E}-\nabla\left(\frac{\mu_e}{\varrho^{(e)}}\right)\right]\tag{9b}$$

$$\mathbf{i}=L_{31}\frac{\nabla T_p}{T_p}+L_{32}\frac{\nabla T_e}{T_e}+L_{33}\left[\mathbf{E}-\nabla\left(\frac{\mu_e}{\varrho^{(e)}}\right)\right]\tag{9c}$$

In Eqs. (9) the quantities $L_{\alpha\beta}$ mean the phenomenological coefficients, which are related to experimental quantities. The transport coefficients $L_{\alpha\beta}$ are related to the thermo-physical properties of the material at hand. In general, the $L_{\alpha\beta}$ depend on the elements of the state space as well as on the thermodynamic forces. In such a case, we are dealing with a nonlinear nonequilibrium theory (NLNET) [24]. If, instead, these coefficients depend only on the elements of the state space, then we face with a semi-linear nonequilibrium theory (SLNET) [24]. Finally, if the $L_{\alpha\beta}$ are constant, then we deal with a linear nonequilibrium theory (LNET) [24]. The coefficients $L_{\alpha\alpha}$ relate the thermodynamic current to its own conjugated thermodynamic force. The cross-coefficients $L_{\alpha\beta}$ with $\alpha\neq\beta$, instead, are representative of the coupling between different physical effects [12, 25]. Any phenomenon in which two or more transport effects are coupled, such as thermal and electrical conductivity, or thermal conductivity and diffusion, is called cross-effect [12, 25].

As the thermoelectric effects arise from the physical interrelation between heat flow and electric current, in the classical thermoelectric models the cross-coefficients $L_{\alpha\beta}$ with $\alpha\neq\beta$, are only related to the coupled transport of heat and electricity. In the present model, instead, the thermoelectric effect is driven by three generalized thermodynamic forces, namely, the phonon and electron temperature gradient and the force due to the electric field and to the chemical potential of the electric charge. As a consequence, the cross-coefficients L_{12} and L_{21} account for the cross effects due to the different temperatures of the heat carriers (which are lacking in the classical case), the coefficients L_{13} and L_{31} represent the coupling between the phonon temperature gradient ad the electric current, and the coefficients L_{23} and L_{32} account for the coupling between the electron temperature gradient ad the electric current. In the standard thermoelectric models, with $T_p = T_e$, we have only two cross-coefficients and a 2×2 transport matrix. Here, instead, we have six cross-coefficients and a 3×3 transport matrix. To be compatible with the second law of thermodynamics (expressed as the positive-definite character of the entropy production) the matrix of phenomenological coefficients $L_{\alpha\beta}$ must be positive definite [12]. On the other hand, the Onsager reciprocal relations [26, 27] ensure that the transport matrix is symmetric, so that the Sylvester criterion concerning the positive definiteness of real-symmetric $n \times n$ matrices is applicable. Such a criterion states that the positiveness of all the leading principal minors of the matrix is necessary and sufficient to ensure that it is positive definite [28].

Recalling that in our theory $\mathbf{q} = \mathbf{q}^{(p)} + \mathbf{q}^{(e)}$, in a somewhat different form the phenomenological equations (9) may be also written as

$$\mathbf{q} = -\left(\lambda_p + \lambda_{ep}\right) \nabla T_p - \left(\lambda_e + \lambda_{pe}\right) \nabla T_e + \left(\frac{\mu_e}{\varrho^{(e)}} + \Pi\right) \mathbf{i} \tag{10a}$$

$$\mathbf{i} = -\sigma_e \epsilon \nabla T_e + \sigma_e \left[\mathbf{E} - \nabla \left(\frac{\mu_e}{\varrho^{(e)}}\right)\right] \tag{10b}$$

once the following identifications are made:

$$\begin{cases} L_{11} = \lambda_p T_p; & L_{12} = \lambda_{pe} T_e; & L_{13} = 0 \\ L_{21} = \lambda_{ep} T_p; & L_{22} = \lambda_e T_e + \sigma_e \varepsilon T_e \Pi; & L_{23} = -\sigma_e \Pi \\ L_{31} = 0; & L_{32} = -\sigma_e \varepsilon T_e; & L_{33} = \sigma_e \end{cases} \tag{11}$$

with Π as the Peltier coefficient, and λ_p and λ_e as the thermal conductivities of the material whenever the sole phonons or electrons [6, 29], respectively, are the heat carriers. It is worth observing that, as the phonon and electron internal energies (or, due to Eqs. (4), the phonon and electron temperatures) enter the state space, our model is developed within the frame of a semi-linear nonequilibrium theory.

Indeed, since we are regarding the phonons and the electrons as constituents of a same mixture of flowing heat carriers, then, in principle, one must take into account the possible interactions between them, which yield further thermal contributions. Therefore, in Eq. (10a) the material functions λ_{pe} and λ_{ep} express those contributions to the total thermal conductivity of the material. Referring the readers to the Appendix for more comments, here we only note that the use of these thermal conductivities, arising from the phenomenological coefficients L_{12} and L_{21} in Eqs. (9a) and (9b), respectively, are representative of the cross effects in the constitutive equations for the diffusive fluxes $\mathbf{q}^{(p)}$ and $\mathbf{q}^{(e)}$. However, as it will be seen in Sec. III, these cross effects do not play any relevant role on the efficiency in the thermoelectric energy conversion, being the difference in the two temperatures the principal responsible for possible enhancements of it.

In Eqs. (11) we assumed $L_{13} = L_{31} = 0$ since it seems logical because the phonons are not expected to be directly sensitive to the external electric field, at least in a first approximation. For polar lattices, this possibility would be open, and L_{13} could be different from zero. However, here we take the simplest expression.

Owing to the Onsager reciprocal relations [26, 27], from Eqs. (11) we obtain

$$\lambda_{pe} = \lambda_{ep} \left(\frac{T_p}{T_e}\right) \tag{12a}$$

$$\Pi = \epsilon T_e \tag{12b}$$

According to the Sylvester's criterion, the additional constraints

$$\lambda_p > 0 \tag{13a}$$

$$\lambda_p \left(\lambda_e + \sigma_e \Pi\right) > \lambda_{pe} \lambda_{ep} \tag{13b}$$

$$\lambda_p \lambda_e > \lambda_{pe} \lambda_{ep} \tag{13c}$$

are necessary and sufficient to ensure that the entropy production is non-negative along arbitrary thermodynamic processes. In fact, due the positive definiteness of the matrix of the transport coefficients, the entropy production is positive whenever at least one thermodynamic force is different from zero, and vanishes when all the thermodynamic forces are zero. Such a situation characterizes the quasi-static (i.e., reversible) processes [30], which correspond to zero entropy production.

The relation (12b) is well known in thermoelectricity when T_e is replaced by T. In that case it is referred to as the *second Kelvin relation*, and it has been used since the early days in the study of thermoelectric phenomena. The different result predicted by Eq. (12b) with respect to the usual statement of the second Kelvin relation (i.e., $\Pi = \epsilon T$) should not be considered as a surprising and unexpected result. In fact, the classical statement is correct in the case that phonons and electrons have the same temperature. In the case they have a different temperatures, instead, the relation (12b) seems more appropriate with respect to the classical form. That result is also not against Onsager reciprocity relations [26, 27] but, on the contrary, it is an illustration of them, more accurate and precise than the classical expression with a single temperature, as it is obtained from the symmetry of coefficients $L_{\alpha\beta}$ appearing in Eqs. (11).

Equation (12b) may be also very useful in practical applications if one is wondering to measure T_p and T_e. In fact, by means of a usual thermometer, one is only able to check the average temperature T, defined by Eq. (5). Equation (12b) turns out that T_e should be given as the ratio between Π and ϵ. Therefore, if one is able to measure Π and ϵ then, by the coupling of Eqs. (5) and (12b), in principle, it will be possible to determine T_p, too. In fact, setting

$$\begin{cases} \alpha = \dfrac{c_v^{(e)}}{c_v}; \ 1-\alpha = \dfrac{c_v^{(p)}}{c_v} \\ \beta_1 = \dfrac{T_e}{T}; \ \beta_2 = \dfrac{T_p}{T} \end{cases} \tag{14}$$

from Eq. (5) we have

$$\alpha\beta_1 + (1-\alpha)\beta_2 = 1 \Leftrightarrow \beta_2 = \frac{1}{1-\alpha} - \left(\frac{\alpha}{1-\alpha}\right)\beta_1 \tag{15}$$

Finally, observing that $\alpha \in \left]0;1\right[$, the physical constraint $\beta_2 > 0$ implies that $\beta_1 \in \left]0;\alpha^{-1}\right[$. From Eq. (15) it is easy to see that the condition $\beta_1 = 1 \Rightarrow \beta_2 = 1$, namely, in this case $T_e \equiv T_p \equiv T$: the two-temperature model described by Eqs. (10) reduces to the usual single-temperature model [3, 11], i.e.,

$$\mathbf{q} = -\lambda\nabla T + \left(\frac{\mu_e}{\varrho^{(e)}} + \Pi\right)\mathbf{i}$$
$$\mathbf{i} = -\sigma_e\epsilon\nabla T + \sigma_e\left[\mathbf{E} - \nabla\left(\frac{\mu_e}{\varrho^{(e)}}\right)\right]$$

once the thermal conductivity λ of the material is supposed to be given as $\lambda = \lambda_p + \lambda_e + 2\lambda_{pe}$. Previous considerations allow us to claim that our model also shows a strong enough physical insight.

III. EFFICIENCY OF THERMOELECTRIC GENERATORS

Research in recent years has been focused on developing both thermoelectric structures, and materials that have high efficiency. In the present section we point out the influence of accounting for two different temperatures in the calculation of the efficiency η of a thermoelectric generator, defined as the ratio between the electric-power output P_{el} and the total heat supplied per unit time $\dot{Q}$, namely,

$$\eta = \frac{P_{\mathrm{el}}}{\dot{Q}} \tag{16}$$

To this end, for the sake of simplicity, we consider a single one-dimensional (y is the sole cartesian coordinate) thermoelectric element of length L under steady conditions. The hot side is held at a temperature T^h (assumed to be the upper side, at $y = L$), and the cold side at the temperature T^c (the lower side, at $y = 0$). We also assume that $\mathbf{i}$ and $\dot{Q}$ enter uniformly into the hot side of the element. In such a situation, the electric-power output is

$$P_{\mathrm{el}} = \mathbf{i} \cdot \int_0^L \mathbf{E}\mathrm{d}y = i\epsilon\left(T_e^h - T_e^c\right) - \frac{i^2 L}{\sigma_e} \tag{17}$$

once the electric field is given by Eq. (10b) with vanishing values of $\nabla\left(\mu_e/\varrho^{(e)}\right)$, for the sake of simplicity, and ϵ and σ_e do not depend on the temperature.

From Eq. (10b), instead, we obtain that the total heat supplied per unit time is

$$\dot{Q} = \int_0^L q\ \mathrm{d}y = \Lambda_p\frac{\left(T_p^h - T_p^c\right)}{L} + \Lambda_e\frac{\left(T_e^h - T_e^c\right)}{L} + \Pi i \tag{18}$$

wherein $\Lambda_p = \lambda_p + \lambda_{ep}$, and $\Lambda_e = \lambda_e + \lambda_{pe}$.

Inserting Eqs. (17) and (18) into Eq. (16) we obtain

$$\eta = \frac{i\epsilon\left(T_e^h - T_e^c\right) - i^2 L\sigma_e^{-1}}{\Lambda_p\left(T_p^h - T_p^c\right)L^{-1} + \Lambda_e\left(T_e^h - T_e^c\right)L^{-1} + \Pi i} \tag{19}$$

If we introduce in Eq. (19) the coefficients β_1 and β_2 defined in Eqs. (14), and take into account Eq. (12b), by straightforward calculations we have

$$\eta = \left(1 - \frac{T^c}{T^h}\right)\left(\frac{\epsilon x - \dfrac{\lambda x^2}{\sigma_e\beta_1}}{\dfrac{\gamma+1}{T^h} + \epsilon x}\right) \Leftrightarrow \eta = \eta_c\eta_r \tag{20}$$

wherein we set $\lambda = \Lambda_p + \Lambda_e$, $\gamma = \left(\Lambda_p/\lambda\right)\left(\beta_2/\beta_1 - 1\right)$, and x is the following ratio between the electric current and the heat flux:

$$x = \frac{iL}{\lambda\left(T^h - T^c\right)} \tag{21}$$

Moreover, in Eq. (20) $\eta_c = 1 - T^c/T^h$ is the usual Carnot efficiency, and η_r is a *reduced efficiency.* Since η_c represents the ideal limit of the thermodynamic efficiency, in practical applications one should find the right way to enhance η_r in order to have a good thermoelectric efficiency. Indeed, it is easy to see that whenever the ratio x defined above gets the value

$$x_{\text{opt}} = \left(\frac{\gamma+1}{\epsilon T}\right)\left(\sqrt{1 + \frac{\bar{Z}T\beta_1}{\gamma+1}} - 1\right) \tag{22}$$

with $\bar{Z} = \epsilon^2\sigma_e/\lambda$, then the reduced efficiency gets its maximum value, and the thermoelectric efficiency reads

$$\eta_{\max} = \eta_c\left[\frac{\bar{Z}T\beta_1 + 2\left(\gamma+1\right)\left(1 - \sqrt{1 + \dfrac{\bar{Z}T\beta_1}{\gamma+1}}\right)}{\bar{Z}T\beta_1}\right] \tag{23}$$

which reduces to the classical form for the maximum thermoelectric efficiency [3, 31] whenever T_p and T_e coincide, i.e., when $\beta_1 = \beta_2 = 1$ and $\gamma = 0$.

From Eq. (23) it easy to recover the usual result that the larger the figure-of-merit, the higher the efficiency of a thermoelectric device.

However, Eq. (23) clearly points out that also the differences between T_p and T_e influence $\eta_{\max}$, whereas the cross effects related to the phenomenological coefficients L_{12} and L_{21} in Eqs. (9a) and (9b) substantially remain unaltered the predictions of our two-temperature model with respect those of the usual single-temperature model. This may be interesting in practical applications, since the most part of the research groups is focusing the attention only on the search of new materials with high values of the figure-of-merit.

In Fig. 1 we plot the behavior of the ratio $\eta_{\max}/\eta_c$ as a function of β_1 for two different values of the nondimensional parameter α, i.e., $\alpha = 0.05$ and $\alpha = 0.5$. For the sake of illustration in our computation we assumed $\Lambda_p = \Lambda_e$, as the materials commonly used in thermoelectric applications show a phonon thermal conductivity which is approximately equal to the electron thermal conductivity. Moreover, we supposed that $\bar{Z}T = 1$.

As it can be seen, the maximum efficiency increases for increasing values of β_1. This means that the bigger T_e with respect to T_p, the better the performances of thermoelectric devices. Indeed, Fig. 1 also allows to analyze the role played by $c_v^{(e)}$ and $c_v^{(p)}$, the latter being usually higher than the former. In fact, it points out that the (positive) slope of the curve $\eta_{\max} = \eta_{\max}\left(\beta_1\right)$ gradually decreases whenever α assumes very small values, whereas it basically takes a constant value when α reaches high enough values, in such a way that whenever $T_e > T_p$, the higher α, the higher $\eta_{\max}$.

At the very end, we observe that in Fig. 1 the value $\eta_{\max}/\eta_c = 0.17$, attained whenever $\beta_1 = 1$ [44] corresponds to the case of a single-temperature model. Thus we may conclude that whenever the electron temperature is higher than the phonon temperature, our two-temperature model yields an efficiency which is higher than that of the usual single-temperature model.

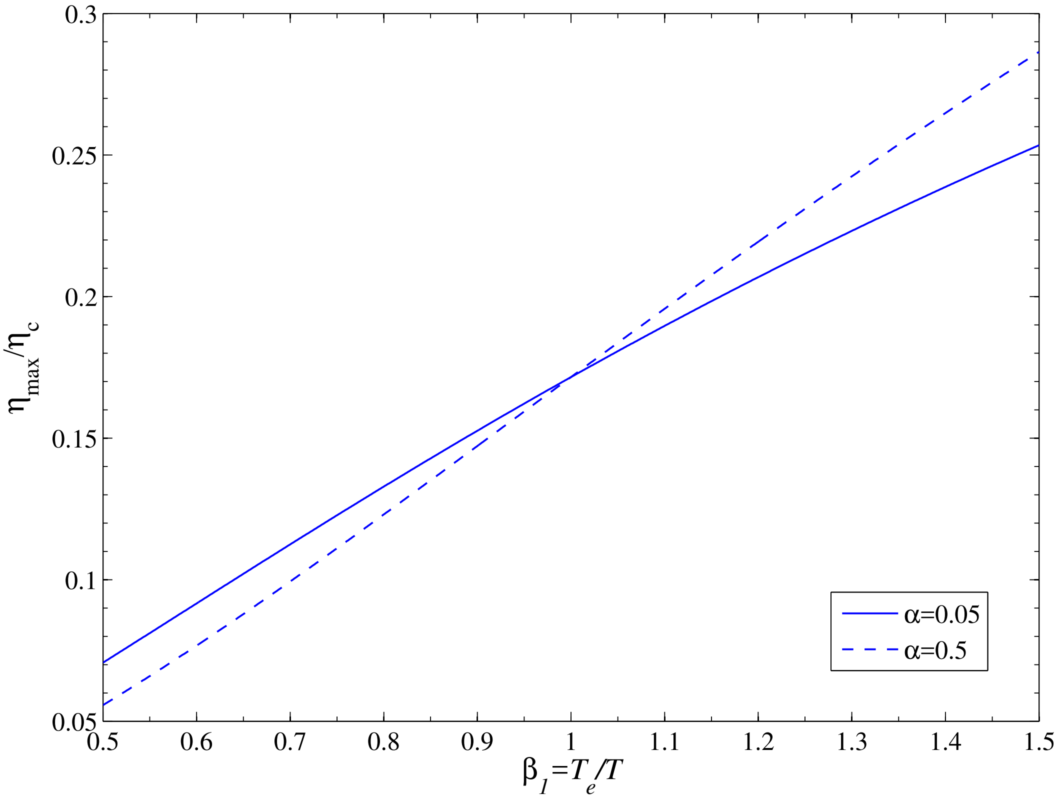

FIG. 1: Behavior of $\eta_{\max}/\eta_{\rm c}$ versus β_1 for two different values of the nondimensional parameter $\alpha = c_v^{(e)}/c_v$: theoretical results arising from Eq. (23). In figure, $\beta_1 < 1 \Rightarrow T_p > T_e$, $\beta_1 = 1 \Rightarrow T_p = T_e$, and $\beta_1 > 1 \Rightarrow T_p < T_e$.

IV. CONCLUSIONS

Thermoelectric devices have gained importance in recent years as viable solutions for appealing applications such as spot cooling of electronic components, remote power generation in space stations and satellites, etc. These solid-state devices have long been known for their reliability, rather than their efficiency. They do not contain moving parts, and their performances primarily rely on the material selection which, indeed, has not yet achieved sufficiently satisfactory candidates for widespread practical applications. Therefore, the research in recent years has been focused on developing both thermoelectric structures, and materials that have higher efficiencies than that of the currently available materials. The advent of nanotechnologies, which allow to improve the actual performances of thermoelectric devices, has shifted the focus towards a deeper understanding of the carrier-transport behavior in nanostructures. In fact, the quantum confinement in nanostructures increases the local-carrier density of states per unit volume near the Fermi energy, yielding an enhancement in the Seebeck coefficient [32], while the thermal conductivity can be decreased due to phonon confinement and phonon scattering [33, 34]. This way, the combined benefits of reduced thermal conductivity and improved Seebeck coefficient imply theoretically higher values of ZT compared to the bulk structures. However, experimental observations have not been able to achieve the presumed benefits of nanostructured thermoelectric devices, despite theoretically predicted improvements.

Owing to the need for a better understanding of the effect of all the significant factors contributing to the thermoelectric figure-of-merit of nanoscale devices, in a previous paper [6] we have investigated the influence of nonlocal effects on it in cylindrical nanowires, and we predicted how Z depends on the features of the transversal section.

Here, instead, we have analyzed the possible consequences of accounting for different temperatures for the different heat carriers which may be interesting in practical applications, as we pointed out in Sec. I and Sec. III. In particular, in the framework of EIT [3, 5], in the present paper we have developed a model of enhanced thermoelectric equations assuming that the population of heat carriers behaves as a mixture of flowing gas particles [6, 13, 14] with different temperatures, according with the theory proposed by Ruggeri and coworkers [20–22]. It seems worth noticing that accounting for different temperatures is also a well-known mechanism of heat conduction in complex materials, where one of the components can be thermally excited independently of the other [7, 8, 35, 36]. In the case of thermoelectric effects, instead, we feel that the consideration of two temperatures is, at least, a theoretical valuable approach because it allows to identify with better conceptual clarity which part of the several effects is directly related to electrons (or holes), which one to phonons, and which one to their mutual interactions. Thus, it is worth to explore it for its own conceptual sake, as a model wider than the usual one, working directly with a single temperature. On the other side, this may open the possibility of new practical strategies, although the effects are expected to be small in usual circumstances. In fact, the results in Eq. (23), arising from the two-temperature model in Eqs. (10), point out that the bigger the electron temperature than the phonon temperature, the higher the performances of a thermoelectric device. This can be clearly seen in Fig. 1 wherein $\eta_{\max}$ increases for enhancing values of the nondimensional ratio $\beta_1 = T_e/T$. Figure 1 also allows us to make a comparison between the theoretical predictions of a single-temperature model ($\beta_1 = 1$) and those of our two-temperature model ($\beta_1 \neq 1$). In particular, whenever T_e is higher than T_p, it points out that the latter model yields a larger efficiency in the thermoelectric energy conversion with respect to that predicted by the former model.

Since from the theoretical point of view it seems very clear the importance of accounting for T_e and T_p, it would be very useful in practical applications to find a possible way to estimate those temperatures [9, 10]. To this end, by observing that our theoretical model predicts that the classical second Kelvin relation breaks down, as stated by Eq. (12b), we also proposed a possible way of checking both temperatures. In more details, we observed that if one is able to measure at nanoscale the Peltier and the Seebeck coefficients separately, then their ratio would turn out, in principle, the electron temperature and then, as a consequence of Eq. (5), the phonon temperature, too. It is worth to note that at nanoscale the different material functions may deviate from their corresponding bulk values, in such a way that several methods of measuring them may be found in literature [37, 38].

From the practical point of view, the way of having a truly different temperature for electrons (and holes) and lattice (phonons) is by means of a pulse-laser excitation yielding its energy to the charged particles (electrons), which later share their energy excess with the lattice. Despite the lattice may be also charged, the much higher mass of the ions makes that the electrons may absorb more energy from the pulse. However, this strategy is not of interest for practical thermoelectric devices, because it would require spending energy on the laser, from which only a part would be taken by the system. A different strategy would be by using a system composed of two (or several) thin layers (as for instance a superlattice) which are shorter than the phonon mean-free path, but larger than the electron mean-free path. If the electron and phonon contributions to the heat flux within the layers are, respectively, $\mathbf{q}^{(e)} = -\lambda_e \nabla T_e$ and $\mathbf{q}^{(p)} = -\lambda_p \nabla T_p$, and the temperature discontinuities at an interface are $\Delta T_e = R_e q_e$ and $\Delta T_p = R_p q_p$, R_e and R_p being the respective thermal resistance of the interface, one may obtain the profile for T_e and T_p along the system. Both temperatures must be equal to the heat baths at the two ends of the whole system, but they may be different from each other along the system. By using suitable materials to have R_e, R_p, λ_e and λ_p (or a suitably reduced effective phonon thermal conductivity), one could have regions with T_e higher than T_p, and regions with T_e lower than T_p. A detailed analysis of both profiles should be carried out to study the global effects of these differences on the efficiency of the thermoelectric conversion in the whole device. Of course, electrons exchange energy with phonons everywhere. Thus, it would be convenient that the electron heat flux is relatively large, in order that this energy exchange does not bring to zero the temperature differences. These effects should be studied in detail. Though the final practical outcome may turn to be small, the new detailed physical understanding of the system would be worth of the effort.

Indeed, in our two-temperature model the problem of measuring T_e and T_p may be also related to the phonon-drag phenomenon [39, 40]. The classical theory of thermoelectricity, in fact, is based on the assumption that the flow of charge carriers and phonons can be treated independently. Under this assumption, the Seebeck coefficient depends solely by the spontaneous electron diffusion. However, when the two flows are linked, the effect of electron-phonon scattering should be taken into account. Hence, in general, the Seebeck coefficient shows two independent contributions: the conventional electron-diffusion contribution and the phonon-drag contribution [40]. The diffusion part is caused by the spatial variation of the electronic occupation in the presence of a thermal gradient, whereas the drag part arises by the interaction between anisotropic lattice vibrations and mobile charge carriers. The overall phonon-drag effect leads to an increase in the Seebeck coefficient. If we look at Eq. (10b), we may observe that it allows to introduce the following effective Seebeck coefficient

$$\epsilon_{\text{eff}} = \epsilon \beta_1 \Leftrightarrow \beta_1 = \frac{\epsilon_{\text{eff}}}{\epsilon} \tag{24}$$

which also allows to claim that the deviation of the effective Seebeck coefficient from its bulk value represents a further possible measurement of the electron temperature. Moreover, along with previous observations about the phonon-drag phenomenon, from Eq. (24) we further claim that in general β_1 should be greater than unit, namely, $T_e > T_p$.

Appendix: compatibility with second law of thermodynamics

The results we derived in the present paper are based upon the system of equations (10). In Sec. II we already pointed out a sufficient set of thermodynamic conditions ensuring the compatibility of those equations with the second law. Indeed, Eqs. (10) follow from the assumption that the specific entropy only depends on the basic variables u_p, u_e and $\varrho^{(e)}$, whereas, according with the general principles of EIT [3, 5, 16, 17], we have assumed that both those variables, and the independent fluxes $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$ and $\mathbf{i}$ belong to the state space. Here we spend more comments about that assumption. In doing this, we take advantage of the second law of thermodynamics.

The second law, accounting for the natural evolution of a system in any possible thermodynamic process, in fact, is a very valuable tool to study the physical consistency of any thermodynamic model. In terms of the entropy density s, its local form reads as in Eq. (7), wherein the entropy source has to be non-negative in any admissible thermodynamic process. Since in Eq. (7) neither s, nor $\mathbf{J}^{(s)}$ belong to the state space, then they have to be expressed through constitutive equations. If we assume for them the very general forms

$$\begin{aligned} &s = s\left(u_p; u_e; \varrho^{(e)}; \mathbf{q}^{(p)}; \mathbf{q}^{(e)}; \mathbf{i}\right) \\ &\mathbf{J}^{(s)} = \mathbf{J}^{(s)}\left(u_p; u_e; \varrho^{(e)}; \mathbf{q}^{(p)}; \mathbf{q}^{(e)}; \mathbf{i}\right) \end{aligned} \tag{25}$$

then, by the chain rule, from Eq. (7) we get

$$\begin{aligned} \sigma^{(s)} = \rho &\left(\frac{\partial s}{\partial u_p}\partial_t u_p + \frac{\partial s}{\partial u_e}\partial_t u_e + \frac{\partial s}{\partial \varrho^{(e)}}\partial_t \varrho^{(e)} + \frac{\partial s}{\partial \mathbf{q}^{(p)}} \cdot \partial_t \mathbf{q}^{(p)} + \frac{\partial s}{\partial \mathbf{q}^{(e)}} \cdot \partial_t \mathbf{q}^{(e)} + \frac{\partial s}{\partial \mathbf{i}} \cdot \partial_t \mathbf{i} \right) \\ &+ \frac{\partial \mathbf{J}^{(s)}}{\partial u_p} \cdot \nabla u_p + \frac{\partial \mathbf{J}^{(s)}}{\partial u_e} \cdot \nabla u_e + \frac{\partial \mathbf{J}^{(s)}}{\partial \varrho^{(e)}} \cdot \nabla \varrho^{(e)} + \frac{\partial \mathbf{J}^{(s)}}{\partial \mathbf{q}^{(p)}} : \nabla \mathbf{q}^{(p)} + \frac{\partial \mathbf{J}^{(s)}}{\partial \mathbf{q}^{(e)}} : \nabla \mathbf{q}^{(e)} + \frac{\partial \mathbf{J}^{(s)}}{\partial \mathbf{i}} : \nabla \mathbf{i} \end{aligned} \tag{26}$$

wherein the colon stands for the double inner product of two matrices. Second law of thermodynamics dictates that the right-hand side of Eq (26) must be nonnegative for arbitrary thermodynamic processes. It contains the higher derivatives $\partial_t u_p$, $\partial_t u_e$, $\partial_t \varrho^{(e)}$, $\partial_t \mathbf{q}^{(p)}$, $\partial_t \mathbf{q}^{(e)}$, $\partial_t \mathbf{i}$, ∇u_p, ∇u_e, $\nabla \varrho^{(e)}$, $\nabla \mathbf{q}^{(p)}$, $\nabla \mathbf{q}^{(e)}$ and $\nabla \mathbf{i}$, which can assume completely arbitrary values [41], as they account for the natural and independent evolution in the space-time of the basic variables u_p, u_e and $\varrho^{(e)}$, as well as for the evolution of the independent fluxes $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$ and $\mathbf{i}$.

The evolution equations of u_p, u_e and $\varrho^{(e)}$ are given by Eqs. (1), whereas the time rates of $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$ and $\mathbf{i}$ in our model read, respectively,

$$\tau_p \partial_t \mathbf{q}^{(p)} + \mathbf{q}^{(p)} = -\lambda_p \nabla T_p - \lambda_{pe} \nabla T_e \tag{27a}$$

$$\tau_e \partial_t \mathbf{q}^{(e)} + \mathbf{q}^{(e)} = -\lambda_{ep} \nabla T_p - \left(\lambda_e + \sigma_e \epsilon \Pi\right) \nabla T_e + \sigma_e \Pi \left[\mathbf{E} - \nabla\left(\frac{\mu_e}{\varrho^{(e)}}\right)\right] + \left(\frac{\mu_e}{\varrho^{(e)}}\right) \mathbf{i} \tag{27b}$$

$$\tau_i \partial_t \mathbf{i} + \mathbf{i} = -\sigma_e \epsilon \nabla T_e + \sigma_e \left[\mathbf{E} - \nabla\left(\frac{\mu_e}{\varrho^{(e)}}\right)\right] \tag{27c}$$

wherein τ_p, τ_e and τ_i are the relaxation times of phonons, electrons and electric current, respectively [6, 42]. In steady-state situations, or whenever those relaxation times are vanishing, from Eqs. (27) it is easy to recover Eqs. (10).

Before to go further in the thermodynamic analysis, we feel that Eqs. (27) deserve some comments. They introduce a theoretical model for thermoelectric effects which allows to point out clearly which part of the several effects is directly related to the different heat/electric carriers, and which one to their mutual interactions. Mutual interactions, in particular, in Eqs. (27a) and (27b) are introduced by cross effects of the form $\lambda_{pe}\nabla T_e$ and $\lambda_{ep}\nabla T_p$, arising from the phenomenological coefficients L_{12} and L_{21} in Eqs. (9) which are peculiar of our two-temperatures model. We already observed that these effects do not play any direct relevant role on the thermoelectric efficiency. They are very important, instead, if one is wondering to determine both the T_p profile and the T_e profile in our system. In fact, since they couple the differential equations for $\mathbf{q}^{(p)}$ and $\mathbf{q}^{(e)}$, then also small perturbations in one temperature have repercussions on the other temperature. However, we note that the analysis of the possible influence of cross effects in the constitutive equations for thermoelectricity is a very interesting research playground, since it may allow to discover new ways to enhance the performances of thermoelectric devices, as it has been pointed out in Ref. [11], for example.

Equations (27) follow from the observation that each thermodynamic flux $\mathbf{J}^{(\alpha)}$ is described by a generalized transport equation of the form [5]

$$\tau_\alpha \partial_t \mathbf{J}^{(\alpha)} + \mathbf{J}^{(\alpha)} = \mathbf{L}_{\alpha\beta} \cdot \mathbf{X}^{(\beta)}$$

wherein $\mathbf{L}_{\alpha\beta}$ is the matrix of the phenomenological coefficients. It is worth observing that whenever the relaxation times τ_p, τ_e and τ_i are negligible, the summation of Eqs. (27a) and (27b) turns out Eq. (10a), whereas Eq. (27c) reduces to Eq. (10b).

To derive the thermodynamic restrictions imposed by the inequality $\sigma^{(s)} \geq 0$, it is possible to follow the procedure proposed by Liu [43] which introduces the constraints in Eqs. (1) and Eqs. (27) by means of suitable Lagrange multipliers, in such a way that the following inequality has to be fulfilled:

$$\begin{aligned}&\sigma^{(s)}-\gamma_p\left(\rho\partial_t u_p+\nabla\cdot\mathbf{q}^{(p)}\right)-\gamma_e\left(\rho\partial_t u_e+\nabla\cdot\mathbf{q}^{(e)}-\mathbf{E}\cdot\mathbf{i}\right)-\gamma_i\left(\rho\partial_t\varrho^{(e)}+\nabla\cdot\mathbf{i}\right)\\&-\boldsymbol{\Gamma}_p\left(\tau_p\partial_t\mathbf{q}^{(p)}+\mathbf{q}^{(p)}+\lambda_p\nabla T_p+\lambda_{pe}\nabla T_e\right)\\&-\boldsymbol{\Gamma}_e\left\{\tau_e\partial_t\mathbf{q}^{(e)}+\mathbf{q}^{(e)}+\lambda_{ep}\nabla T_p+\left(\lambda_e+\sigma_e\epsilon\Pi\right)\nabla T_e-\sigma_e\Pi\left[\mathbf{E}-\nabla\left(\frac{\mu_e}{\varrho^{(e)}}\right)\right]-\left(\frac{\mu_e}{\varrho^{(e)}}\right)\mathbf{i}\right\}\\&-\boldsymbol{\Gamma}_i\left\{\tau_i\partial_t\mathbf{i}+\mathbf{i}+\sigma_e\epsilon\nabla T_e-\sigma_e\left[\mathbf{E}-\nabla\left(\frac{\mu_e}{\varrho^{(e)}}\right)\right]\right\}\geq 0\end{aligned}\tag{28}$$

Since the Lagrange multipliers γ_p, γ_e, γ_i, $\boldsymbol{\Gamma}_p$, $\boldsymbol{\Gamma}_e$ and $\boldsymbol{\Gamma}_i$ are well-defined on the state space [41], as consequence of the coupling of Eq. (26) and inequality (28), thermodynamic restrictions ensue by nullifying the coefficients of the higher derivatives [41].

In particular, setting equal to zero each coefficient of the time-derivatives of the state-space variables, one has:

$$\frac{\partial s}{\partial u_p}=\gamma_p \Leftrightarrow \frac{1}{T_p}=\gamma_p \tag{29a}$$

$$\frac{\partial s}{\partial u_e}=\gamma_e \Leftrightarrow \frac{1}{T_e}=\gamma_e \tag{29b}$$

$$\frac{\partial s}{\partial \varrho^{(e)}}=\gamma_i \Leftrightarrow -\frac{\mu_e}{\varrho^{(e)}T_e}=\gamma_i \tag{29c}$$

$$\frac{\partial s}{\partial \mathbf{q}^{(p)}}=\frac{\boldsymbol{\Gamma}_p\tau_p}{\rho} \tag{29d}$$

$$\frac{\partial s}{\partial \mathbf{q}^{(e)}}=\frac{\boldsymbol{\Gamma}_e\tau_e}{\rho} \tag{29e}$$

$$\frac{\partial s}{\partial \mathbf{i}}=\frac{\boldsymbol{\Gamma}_i\tau_i}{\rho} \tag{29f}$$

These relations turn out useful information about the dependence of the specific entropy on the state-space variables. A possible form of s compatible both with the principle of maximum entropy at the equilibrium, and with Eqs. (29) is

$$s=s_0\left(u_p;u_e;\varrho^{(e)}\right)-\frac{\tau_p}{2\Lambda_p T_p^2}\mathbf{q}^{(p)}\cdot\mathbf{q}^{(p)}-\frac{\tau_e}{2\left(\Lambda_e+\epsilon\Pi\sigma_e\right)T_e^2}\mathbf{q}^{(e)}\cdot\mathbf{q}^{(e)}-\frac{\tau_i}{2\epsilon\sigma_e T_e^2}\mathbf{i}\cdot\mathbf{i} \tag{30}$$

provided the following identifications are made:

$$\boldsymbol{\Gamma}_p=\frac{\rho}{2\Lambda_p T_p^2}\mathbf{q}^{(p)} \tag{31a}$$

$$\boldsymbol{\Gamma}_e=\frac{\rho}{2\left(\Lambda_e+\epsilon\Pi\sigma_e\right)T_e^2}\mathbf{q}^{(e)} \tag{31b}$$

$$\boldsymbol{\Gamma}_i=\frac{\rho}{2\epsilon\sigma_e T_e^2}\mathbf{i} \tag{31c}$$

From Eq. (30) it follows that whenever the relaxation times τ_p, τ_e and τ_i are negligible, then the dependence of s on the fluxes $\mathbf{q}^{(p)}$, $\mathbf{q}^{(e)}$ and $\mathbf{i}$ may be neglected as well, and one may assume $s\approx s_0\left(u_p;u_e;\varrho^{(e)}\right)$. The result above proves that the Gibbs equation (3), postulated in Sec. II, is in accordance with second law of thermodynamics.

Moreover, if one sets equal to zero the coefficients of the the first-order spatial derivatives of the state-space variables, the following further set of thermodynamic restrictions ensues:

$$\frac{\partial \mathbf{J}^{(s)}}{\partial u_p} c_v^{(p)} = \mathbf{\Gamma}_p \lambda_p + \mathbf{\Gamma}_e \left[\lambda_{ep} + \sigma_e \Pi \frac{\partial}{\partial u_p} \left(\frac{\mu_e}{\varrho^{(e)}} \right) \right] + \mathbf{\Gamma}_i \sigma_e \frac{\partial}{\partial u_p} \left(\frac{\mu_e}{\varrho^{(e)}} \right) \tag{32a}$$

$$\frac{\partial \mathbf{J}^{(s)}}{\partial u_e} c_v^{(e)} = \mathbf{\Gamma}_p \lambda_{pe} + \mathbf{\Gamma}_e \left\{ \lambda_e + \sigma_e \Pi \left[\epsilon + \frac{\partial}{\partial u_e} \left(\frac{\mu_e}{\varrho^{(e)}} \right) \right] \right\} + \mathbf{\Gamma}_i \sigma_e \left[\epsilon + \frac{\partial}{\partial u_e} \left(\frac{\mu_e}{\varrho^{(e)}} \right) \right] \tag{32b}$$

$$\frac{\partial \mathbf{J}^{(s)}}{\partial \varrho^{(e)}} = \sigma_e \left(\Pi \mathbf{\Gamma}_e + \mathbf{\Gamma}_i \right) \frac{\partial}{\partial \varrho^{(e)}} \left(\frac{\mu_e}{\varrho^{(e)}} \right) \tag{32c}$$

$$\frac{\partial \mathbf{J}^{(s)}}{\partial \mathbf{q}^{(p)}} = \gamma_p \mathbf{U} \tag{32d}$$

$$\frac{\partial \mathbf{J}^{(s)}}{\partial \mathbf{q}^{(e)}} = \gamma_e \mathbf{U} \tag{32e}$$

$$\frac{\partial \mathbf{J}^{(s)}}{\partial \mathbf{i}} = \gamma_i \mathbf{U} \tag{32f}$$

with $\mathbf{U}$ being the unitary matrix.

It is easy to verify by direct substitution that the system of thermodynamic restrictions (32) admits as solution the constitutive equation (8a).

These thermodynamic considerations allow to claim that the model equations (10), which are a particular case of the more general equations (27), are in accordance with the basic principles of continuum physics.

Acknowledgements

A. S. acknowledges the University of Basilicata for funding the research project *Modeling heat and electric transport in nanosystems in the presence of memory, nonlocal and nonlinear effects*, and the Italian *Gruppo Nazionale per la Fisica Matematica - GNFM* for financial support under grant *Progetto Giovani 2012*.

V. A. C. acknowledges financial support of the Italian *Gruppo Nazionale per la Fisica Matematica - GNFM*. Thanks are given to the University of Basilicata for financial support and for funding the research subject in Mathematical Physics *Equazioni costitutive per la conduzione del calore nei nanosistemi.*

D. J. acknowledges the financial support from the *Dirección General de Investigación* of the Spanish Ministry of Science and Innovation under grant FIS No. 2009-13370-C02-01, the *Consolider Project NanoTherm* (grant CSD-2010-00044), and the *Direcció General de Recerca* of the Generalitat of Catalonia under grant No. 2009-SGR-00164.

---

[1] D. Y. Tzou, *Macro to micro-scale heat transfer. The lagging behaviour.* New York: Taylor and Francis, 1997.
[2] Z. M. Zhang, *Nano/Microscale heat transfer.* New York: McGraw-Hill, 2007.
[3] G. Lebon, D. Jou, and J. Casas-Vázquez, *Understanding nonequilibrium thermodynamics.* Berlin: Springer, 2008.
[4] S. Volz (ed.), *Thermal Nanosystems and Nanomaterials (Topics in Applied Physics).* Berlin: Springer, 2010.
[5] D. Jou, J. Casas-Vázquez, and G. Lebon, *Extended Irreversible Thermodynamics.* Berlin: Springer, fourth revised ed., 2010.
[6] A. Sellitto, V. A. Cimmelli, and D. Jou, "Thermoelectric effects and size dependency of the figure-of-merit in cylindrical nanowires," *Int. J. Heat Mass Transfer*, vol. 57, pp. 109–116, 2013.
[7] D. Jou, A. Sellitto, and V. A. Cimmelli, "Phonon temperature and electron temperature in thermoelectric coupling," *J. Non-Equilib. Thermodyn.*, vol. 38, pp. 335–361, 2013.
[8] D. Jou, A. Sellitto, and V. A. Cimmelli, "Multi-temperature mixture of phonons and electrons and nonlocal thermoelectric transport in thin layers," *Int. J. Heat Mass Transfer*, vol. 71, pp. 459–468, 2014.
[9] S. Berciaud, M. Y. Han, K. F. Mak, L. E. Brus, P. Kim, and T. F. Heinz, "Electron and optical phonon temperatures in electrically biased graphene," *Phys. Rev. Lett.*, vol. 104, p. 227401 (4 pages), 2010.
[10] M. Schreier, A. Kamra, M. Weiler, J. Xiao, G. E. W. Bauer, R. Gross, and S. T. B. Goennenwein, "Magnon, phonon, and electron temperature profiles and the spin Seebeck effect in magnetic insulator/normal metal hybrid structures," *Phys. Rev. B*, vol. 88, p. 094410, 2013.
[11] A. Sellitto, "Crossed nonlocal effects and breakdown of the Onsager symmetry relation in a thermodynamic description of thermoelectricity," *Physica D*, vol. 243, pp. 53–61, 2014.
[12] S. R. De Groot and P. Mazur, *Nonequilibrium Thermodynamics.* Amsterdam: North-Holland Publishing Company, 1962.

[13] G. Chen, *Nanoscale Energy Transport and Conversion - A Parallel Treatment of Electrons, Molecules, Phonons, and Photons.* Oxford: Oxford University Press, 2005.

[14] F. X. Alvarez, D. Jou, and A. Sellitto, "Phonon hydrodynamics and phonon-boundary scattering in nanosystems," *J. Appl. Phys.*, vol. 105, p. 014317 (5 pages), 2009.

[15] B. D. Coleman and E. H. Dill, "Thermodynamic restrictions on the constitutive equations of electromagnetic theory," *ZAMP*, vol. 22, pp. 691–702, 1971.

[16] G. Lebon, "Heat conduction at micro and nanoscales: A review through the prism of Extended Irreversible Thermodynamics," *J. Non-Equilib. Thermodyn.*, vol. 39, pp. 35–59, 2014.

[17] V. A. Cimmelli, D. Jou, T. Ruggeri, and P. Ván, "Entropy Principle and Recent Results in Non-Equilibrium Theories," *Entropy*, vol. 16, pp. 1756–1807, 2014.

[18] Z. Lin, L. V. Zhigilei, and V. Celli, "Electron-phonon coupling and electron heat capacity of metals under conditions of strong electron-phonon nonequilibrium," *Phys. Rev. B*, vol. 77, p. 075133 (17 pages), 2008.

[19] L. X. Benedict, S. G. Louie, and M. L. Cohen, "Heat capacity of carbon nanotubes," *Solid State Commun.*, vol. 100, pp. 177–180, 1996.

[20] H. Gouin and T. Ruggeri, "Identification of an average temperature and a dynamical pressure in a multitemperature mixture of fluids," *Phys. Rev. E*, vol. 78, p. 016303 (7 pages), 2008.

[21] T. Ruggeri and J. Lou, "Heat conduction in multi-temperature mixtures of fluids: the role of the average temperature," *Phys. Lett. A*, vol. 373, pp. 3052–3055, 2009.

[22] T. Ruggeri, "Multi-temperature mixture of fluids," *Theoret. Appl. Mech.*, vol. 36, pp. 207–238, 2009.

[23] I. Gyarmati, *Nonequilibrium Thermodynamics.* Berlin: Springer, 1970.

[24] I. Gyarmati, "On the wave approach of thermodynamics and some problems of non-linear theories," *J. Non-Equilib. Thermodyn.*, vol. 2, pp. 236–260, 1977.

[25] Y. D. adn I. Sandler, "Linear-nonequilibrium thermodynamics theory for coupled heat and mass transport," *Int. J. Heat Mass Transf.*, vol. 44, pp. 2439–2451, 2001.

[26] L. Onsager, "Reciprocal relations in irreversible processes I," *Phys. Rev.*, vol. 37, pp. 405–426, 1931.

[27] L. Onsager, "Reciprocal relations in irreversible processes II," *Phys. Rev.*, vol. 38, pp. 2265–2279, 1931.

[28] G. T. Gilbert, "Positive Definite Matrices and Sylvester's Criterion," *The American Mathematical Monthly*, vol. 08, pp. 44–46, 1991.

[29] N. Stojanovic, D. H. S. Maithripala, J. M. Berg, and M. Holtz, "Thermal conductivity in metallic nanostructures at high temperature: electrons, phonons, and the Wiedemann-Franz law," *Phys. Rev. B*, vol. 82, p. 075418 (9 pages), 2010.

[30] M. W. Zemanski and R. H. Dittman, *Heat and Thermodynamics.* New York: MacGraw-Hill, seventh revised ed., 1997.

[31] G. Benenti, K. Saito, and G. Casati, "Thermodynamic bounds on efficiency for systems with broken time-reversal symmetry," *Phys. Rev. Lett.*, vol. 106, p. 230602 (4 pages), 2011.

[32] L. D. Hicks and M. S. Dresselhaus, "Effect of quantum-well structures on the thermoelectric figure of merit," *Phys. Rev. B*, vol. 47, pp. 12727–12731, 1993.

[33] A. Balandin and K. L. Wang, "Effect of phonon confinement on the thermoelectric figure of merit of quantum wells," *J. Appl. Phys.*, vol. 84, p. 6149 (5 pages), 1998.

[34] A. Balandin and K. L. Wang, "Significant decrease of the lattice thermal conductivity due to phonon confinement in a free-standing semiconductor quantum well," *Phys. Rev. B*, vol. 58, pp. 1544–1549, 1998.

[35] S. I. Anisimov, B. L. Kapeliovich, and T. L. Perel'man, "Electron emission from metal surfaces exposed to ultrashort laser pulses," *Sov. Phys. JETP*, vol. 39, p. 375, 1974.

[36] P. Ván and T. Fülöp, "Universality in heat conduction theory: weakly nonlocal thermodynamics," *Ann. Phys.*, vol. 524, pp. 470–478, 2012.

[37] H. Straube, J.-M. Wagner, and O. Breitenstein, "Measurement of the Peltier coefficient of semiconductors by lock-in thermography," *Appl. Phys. Lett.*, vol. 95, p. 052107 (3 pages), 2009.

[38] S. Iwanaga, E. S. Toberer, A. La Londe, and G. J. Snyder, "A high temperature apparatus for measurement of the Seebeck coefficient," *Rev. Sci. Instrum.*, vol. 82, p. 063905, 2011.

[39] A. Bulusu and D. Walker, "Review of electronic transport models for thermoelectric materials," *Superlattices and Microstructures*, vol. 44, pp. 1–36, 2008.

[40] M. Pokharela, H. Zhaoa, K. Lukasa, Z. Rena, C. Opeila, and B. Mihaila, "Phonon drag effect in nanocomposite $FeSb_2$," *MRS Communications*, vol. 3, pp. 31–36, 2013.

[41] V. A. Cimmelli, A. Sellitto, and V. Triani, "A new thermodynamic framework for second-grade Korteweg-type viscous fluids," *J. Math. Phys.*, vol. 50, p. 053101 (16 pages), 2009.

[42] P. E. Hopkins, P. M. Norris, L. M. Phinney, S. A. Policastro, and R. G. Kelly, "Thermal Conductivity in Nanoporous Gold Films during Electron-Phonon Nonequilibrium," *J. of Nanomaterials*, vol. 2008, p. 418050 (7 pages), 2008.

[43] I.-S. Liu, "Method of Lagrange multipliers for exploitation of entropy principle," *Arch. Rational Mech. Anal.*, vol. 46, pp. 131–138, 1972.

[44] Along with previous observations in this case one also has $\beta_2 = 1$, and moreover $\gamma = 0$